

## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>J2069 (C) RJG</b>	<b>FOR FURTHER ACTION</b> see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No. <b>PCT/EP2004/003032</b>	International filing date (day/month/year) <b>19/03/2004</b>	(Earliest) Priority Date (day/month/year) <b>03/04/2003</b>
Applicant  <b>UNILEVER PLC</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ The international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. 1.

2. ☐ **Certain claims were found unsearchable** (See Box II).

3. ☐ **Unity of invention is lacking** (see Box III).

**4. With regard to the title,**

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

**5. With regard to the abstract,**

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

**6. With regards to the drawings,**

- a. the figure of the **drawings** to be published with the abstract is Figure No. \_\_\_\_\_

☐ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

- b. ☐ none of the figures is to be published with the abstract.

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D17/02 C11D3/20 C11D9/26

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 848 056 A (KAO CORP) 17 June 1998 (1998-06-17) cited in the application page 4, columns 43-49; claim 11 page 2, lines 41-43, 50-57	1-13
A	WO 01/88079 A (HENKEL KGAA ; SEMRAU MARKUS (DE); BIRNBRICH PAUL (DE); RAEHSE WILFRIED) 22 November 2001 (2001-11-22) page 2, paragraph 4-6; claims 37-55; examples 1-3 page 6, lines 2,5 page 10, paragraph 3 - page 11, paragraph 6	1-12
A	US 5 895 780 A (STEPHENSON JOSEPH ET AL) 20 April 1999 (1999-04-20) column 2, line 44 - column 3, line 17	1
-/--		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

22 June 2004

Date of mailing of the international search report

02/07/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

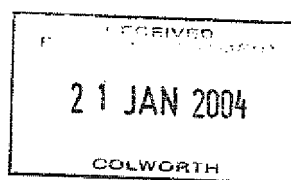
Authorized officer

Klier, E

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 239 027 A (KAO CORP) 11 September 2002 (2002-09-11) paragraphs '0001!', '0004!; claims 1-7; table 1 -----	1
A	EP 0 413 284 A (COLGATE PALMOLIVE CO) 20 February 1991 (1991-02-20) cited in the application page 2, lines 4-6,38-44; claims 4-7; examples 1-4 -----	1

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0848056	A	17-06-1998	JP 3227694 B2	12-11-2001
			JP 10168494 A	23-06-1998
			DE 69717060 D1	19-12-2002
			DE 69717060 T2	31-07-2003
			EP 0848056 A2	17-06-1998
			ID 18829 A	14-05-1998
			TW 530086 B	01-05-2003
			US 5972860 A	26-10-1999
WO 0188079	A	22-11-2001	DE 10107217 A1	22-11-2001
			AU 9521601 A	26-11-2001
			WO 0188079 A1	22-11-2001
			EP 1287109 A1	05-03-2003
			JP 2004510838 T	08-04-2004
			US 2004053808 A1	18-03-2004
US 5895780	A	20-04-1999	US 5602088 A	11-02-1997
EP 1239027	A	11-09-2002	EP 1239027 A1	11-09-2002
			CN 1392899 T	22-01-2003
			WO 0224858 A1	28-03-2002
			JP 2002167599 A	11-06-2002
EP 0413284	A	20-02-1991	US 5017302 A	21-05-1991
			AU 635552 B2	25-03-1993
			AU 6019790 A	21-02-1991
			BR 9004021 A	03-09-1991
			CA 2022994 A1	16-02-1991
			CS 9003980 A3	15-01-1992
			DD 297185 A5	02-01-1992
			EP 0413284 A2	20-02-1991
			GR 90100593 A, B	30-12-1991
			HU 54730 A2	28-03-1991
			IE 902939 A1	27-02-1991
			JP 3221600 A	30-09-1991
			MX 163863 B	26-06-1992
			NO 903566 A	18-02-1991
			NZ 234865 A	26-08-1993
			PT 94983 A	18-04-1991
			ZA 9006192 A	29-04-1992



Application No: GB 0317257.4  
Claims searched: 1-13

Examiner: Michael Conlon  
Date of search: 15 January 2004

## Patents Act 1977 : Search Report under Section 17

### Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance	
X	1-13	US5194172	PROCTER & GAMBLE column 4 lines 5-16, column 5 lines 29-33
A	-	US2002/0198120 A1	KODUVELY
A	-	US5017302	COLGATE-PALMOLIVE

### Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

### Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC<sup>W</sup>:

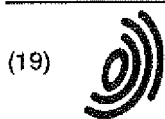
C5D

Worldwide search of patent documents classified in the following areas of the IPC<sup>7</sup>:

C11D

The following online and other databases have been used in the preparation of this search report:

Online: WPI EPODOC JAPIO



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) EP 0 848 056 A2

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:

17.06.1998 Bulletin 1998/25

(51) Int. Cl.<sup>6</sup>: C11D 10/04, C11D 17/00

// C11D1:74, C11D1:72

(21) Application number: 97121828.4

(22) Date of filing: 11.12.1997

(84) Designated Contracting States:

AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 11.12.1996 JP 352215/96

(71) Applicant: Kao Corporation

Chuo-Ku Tokyo 103 (JP)

(72) Inventors:

- Eshita, Yoshiyuki  
Sumida-ku, Tokyo 131 (JP)

• Tonomura, Manabu

Sumida-ku, Tokyo 131 (JP)

• Nozaki, Toshio

Sumida-ku, Tokyo 131 (JP)

• Otani, Hironobu

Sumida-ku, Tokyo 131 (JP)

• Hasegawa, Takeshi

Sumida-ku, Tokyo 131 (JP)

(74) Representative:

Hansen, Bernd, Dr. Dipl.-Chem. et al

Hoffmann Eitle,

Patent- und Rechtsanwälte,

Arabellastrasse 4

81925 München (DE)

(54) Framed soap composition

(57) A framed soap composition comprises (a) from 20 to 50% by weight of a fatty acid soap, (b) from 1 to 15% by weight of a nonionic surfactant, and (c) from 0.1 to 5% by weight of an inorganic salt. A framed soap composition incorporated with air bubbles is produced by melting a mixture containing these components while heating the mixture in the presence of water, subjecting the resultant molten material to aeration treatment to incorporate air bubbles, and pouring the resultant molten material incorporated with air bubbles, into a frame followed by cooling to harden the molten material.

EP 0 848 056 A2

## Description

BACKGROUND OF THE INVENTION

## 1. Field of the Invention

This invention relates to a framed soap composition having advantages that it may hardly crack and also hardly become swollen, even when any means is taken for its formulation, e.g., activators other than soap are added, in order to attain a preferable feel on use, and also having a high productivity comparable to milled soap.

## 2. Description of the Related Art

From differences in production processes, soap can be roughly grouped into two types. One of them is milled soap and the other is framed soap.

The milled soap is obtained by adding a perfume, a dye and so forth to a soap base material obtained by heating and drying neat soap, well mixing them by means of a mixer, putting the resultant mixture to a rolling machine and an extruder to extrude and mold the mixture into bars while kneading and compressing it, and stamping the bar-like molded products thus obtained. The milled soap obtained in this way have advantages that it may readily dissolve in water or the like and also has a high productivity. On the other hand, however, the milled soap has problems that it tends to crack and tends to become swollen. In particular, it greatly tends to become swollen when it has a high water content or when it contains other activators.

As for the framed soap, it is obtained by adding various additives to neat soap, directly pouring the resultant mixture into a frame, and cooling it in the frame to harden, followed by drying. The framed soap obtained in this way is constituted basically of from 50 to 70% by weight of fatty acid soap, from 10 to 20% by weight of polyols (glycerol, etc.) and the balance being water, and has features that it may hardly crack and may hardly become swollen. Also, since it can be produced basically by pouring the neat soap into a frame, it can be produced at a lower cost in view of the cost of production facilities than the cost of production facilities for the milled soap.

The framed soap, however, has disadvantages that it takes at least a day or two days until the soap hardens and dries, and takes as long as about a month in the case of transparent soap, bringing about a problem of a very low productivity. For this reason, under existing circumstances, the framed soap has commercially a very small share except for transparent soap, despite the advantages that it may hardly crack and may hardly become swollen. This is because, as stated above, while it can be produced at a lower cost than the milled soap in view of the cost of production facilities than the cost of production facilities for the milled soap, its final products result in a greatly higher cost of production than the milled soap.

What is called light-weight soap or floating soap, in which air bubbles are entrapped, is also known as a type of the framed soap, see Japanese Patent Application Laid-open No. 4-218599. This publication discloses a floating soap produced by melting a neat soap composed of from 10 to 50% of coconut oil and 50 to 90% of beef tallow and having a water content of from 28 to 35%, introducing the resultant molten material into a high-shear mixing machine, blowing and mixing high-pressure air to incorporate air bubbles into the molten material, pouring into a soap frame the resultant mixture incorporated with air bubbles, and leaving it to cool to harden.

However, the formulation of soap as disclosed in Japanese Patent Application Laid-open No. 4-218599 has caused a problem that the bubbles can not be well retained as they stand to cause phase separation into crushed bubble phase and solid phase to become hard.

SUMMARY OF THE INVENTION

The present invention will solve the above problems the prior art has had. Accordingly, a first object of the present invention is to make it possible to produce framed soap that may hardly crack and may hardly become swollen, in a productivity comparable to that of the milled soap.

A second object of the present invention is to make it possible to produce bubble-entrapped soap in which air bubbles are incorporated at a high volume fraction, which can be readily produced by framing.

The present inventors have discovered that a molten material of a mixture prepared by mixing a fatty acid soap with a nonionic surfactant and an inorganic salt in a specific proportion, melted in the presence of water can be hardened in a short time when this molten material is poured into a frame followed by cooling, and also discovered that such a molten material can be readily treated by aeration using a conventional whipping machine and also the resultant molten material incorporated with air bubbles can be hardened in a short time as it stands when it is poured into a frame followed by cooling. Thus, they have accomplished the present invention.

As a first embodiment which can achieve the first object, the present invention provides a framed soap composition

comprising the following components (a) to (c):

- (a) from 20 to 50% by weight of a fatty acid soap;
- (b) from 1 to 15% by weight of a nonionic surfactant; and
- (c) from 0.1 to 5% by weight of an inorganic salt.

As a second embodiment which can achieve the second object, the present invention provides a process for producing a framed soap composition incorporated with air bubbles, comprising the steps of;

melting a mixture containing the following components (a) to (c):

- (a) from 20 to 50% by weight of a fatty acid soap;
- (b) from 1 to 15% by weight of a nonionic surfactant; and
- (c) from 0.1 to 5% by weight of an inorganic salt;

while heating the mixture in the presence of water to obtain a molten material; subjecting the molten material to aeration treatment to incorporate air bubbles to obtain a molten material incorporated with air bubbles; and pouring the molten material incorporated with air bubbles, into a frame followed by cooling to harden the molten material.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a perspective view of a cup-like container used as a soap frame in Example 7.

Fig. 2 illustrates how the framed soap composition prepared in Example 7 stands in its cross section.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described below in detail.

According to the first embodiment, the present invention is a framed soap composition comprising the following components (a) to (c):

- (a) from 20 to 50% by weight of a fatty acid soap;
- (b) from 1 to 15% by weight of a nonionic surfactant; and
- (c) from 0.1 to 5% by weight of an inorganic salt.

With such formulation, a molten material of a mixture of these, melted in the presence of water can be hardened in a short time when the molten material is poured into a frame followed by cooling, so that a high productivity comparable to that of milled soap can be attained.

The framed soap composition according to the second embodiment of the present invention, having the same formulation as the first embodiment of the present invention, is obtained by whipping the molten material before it is poured into a frame, to make aeration treatment. Such treatment makes the hardening rate much higher. Accordingly, when the molten material in a whipped state is poured into the frame, it can be hardened as it is, without causing phase separation.

In this instance, taking account of the hardening rate, hardness, easy dissolution and so forth of the soap composition, the air bubbles may preferably be in a volume fraction of at least 10%, and more preferably at least 30%. From the viewpoint of the strength of the resultant soap composition, the air bubbles may preferably be in a volume fraction not more than 80%.

As to the size of air bubbles, in order to make the framed soap composition not excessively dissolve and also make it hard to become swollen, the air bubbles may preferably be in an average bubble diameter of 80  $\mu\text{m}$  or smaller, and more preferably be 60  $\mu\text{m}$  or smaller. Here are no particular limitations on the lower limit of the average bubble diameter. Taking account of productivity when a conventional whipping machine for industrial use is used, it may preferably be 10  $\mu\text{m}$  or larger, and more preferably 20  $\mu\text{m}$  or larger.

As the gas used when the aeration treatment is made, air, nitrogen gas or the like may be used under appropriate selection.

The whipping carried out as described above enables the framed soap composition to have a good white appearance even when any whitener such as titanium oxide is not used. Also, when colored, the soap can have a preferable pale color tone. Moreover, the soap can be well fragrant when used, making it possible to use perfumes in a smaller quantity. Furthermore, the properties of being hard to crack and the properties of being hard to become swollen which



are inherent in framed soap compositions can be ensured.

The component-(a) fatty acid soap used in the first and second embodiments of the present invention may include those selected from the group consisting of alkali metal salts (e.g., sodium salt and potassium salts), ammonium salts or alkanol amine salts (e.g., monoethanolamine salts, diethanolamine salts and triethanolamine salts) of saturated or unsaturated fatty acids having 8 to 22 carbon atoms. In particular, the component-(a) fatty acid may preferably contain an alkali metal salt, especially, a sodium salt of a saturated fatty acid in a proportion of at least 80% by weight, because the soap composition may harden with difficulty if the saturated fatty acid is in a small proportion in the component-(a) fatty acid soap. Here, in order to improve lathering properties of the framed soap composition, the component-(a) fatty acid soap may preferably contain lauric acid soap in a proportion of at least 25% by weight.

The fatty acid constituting the component-(a) fatty acid soap may include those obtained from vegetable fats and oils or animal fats and oils, e.g., palm oil, palm kernel oil, coconut oil, castor oil, soy bean oil, cotton seed oil, rapeseed oil, sunflower oil, beef tallow and lard. In particular, palm kernel oil or coconut oil is preferred. In this instance, these fats and oils may preferably be previously subjected to hydrogenation so that they can have a low degree of unsaturation.

The component-(a) fatty acid soap can be produced by direct saponification of the above fats and oils or by neutralization of free fatty acids separately prepared.

The component-(a) fatty acid soap must be contained in the framed soap composition in an amount of at least 20% by weight, taking account of lathering properties and hardening properties. If it is in a too large content, other components relatively come to be in a too small content to obtain the desired properties. Hence, it should be in a content up to 50% by weight, and may preferably be in a content of from 25 to 45% by weight.

The component-(b) nonionic surfactant used in the first and second embodiments of the present invention is used in order to accelerate the hardening of the soap composition, and may be used under appropriate selection from known nonionic surfactants. In particular, preferred nonionic surfactants may include polyoxyethylene (POE) fatty acid esters and polyoxyethylene alkyl ethers, and may specifically include compounds having as a hydrophilic group a polyoxyethylene group having an average number of EO (ethylene oxide) addition moles of from 6 to 150, and preferably from 10 to 50. Of such compounds, compounds having as a hydrophobic group an alkyl group having 10 to 18 carbon atoms, preferably 12 to 14 carbon atoms, and having an HLB (hydrophilic-lipophilic balance) value of 8 or more, and preferably 10 or more, are preferred. For example, as preferred examples, they may include EMANONE 1112 (polyethylene glycol(12) monolaurate available from Kao Corporation; HLB: 14.8), EMULGEN 123P (polyethylene(23) lauryl ether available from Kao Corporation; HLB: 16.9), and EMALOX 730 (polyethylene(30) lauryl ether available from Nihon Emulsion Co., Ltd.; HLB: 18).

The component-(b) nonionic surfactant may be contained in the framed soap composition in an amount of from 1 to 15% by weight, and preferably from 2 to 4% by weight.

The component-(a) fatty acid soap and the component-(b) nonionic surfactant may preferably be contained in a ratio ranging from 1:25 to 1:5, and more preferably 1:20 to 1:10. If the fatty acid soap is in a too large content with respect to the nonionic surfactant, its addition can be effective with difficulty, and, if in a too small content, the soap composition can not have a sufficient hardness.

The component-(c) inorganic salt used in the first and second embodiments of the present invention imparts a good fluidity to the soap composition when the molten material for the framed soap composition is poured into the frame. As a preferable inorganic salt, it may include sodium chloride. The component-(c) inorganic salt may be contained in the framed soap composition in an amount of from 0.1 to 5% by weight, and preferably from 1 to 4% by weight. If it is less than 0.1% by weight, crystals of soap may grow in the form of fibers to cause an increase in viscosity to provide no intended fluidity. If more than 5% by weight, the lathering properties may lower undesirably.

In addition to the above components, the framed soap compositions according to the first and second embodiments of the present invention may preferably contain a polyol, e.g., glycerol, sorbitol, xylitol, mannitol, sucrose, glucose, trehalose, polyethylene glycol, polypropylene glycol and water-soluble polymers. The polyol can improve the stability of air bubbles present in the molten material of the components (a) to (b). Such a polyol may preferably be contained in the framed soap composition in an amount of from 5 to 40% by weight, and more preferably from 20 to 30% by weight. If it is in a too small content, the air bubbles can not be made well stable, and, if it is in a too large content, the soap composition may harden with difficulty.

In the case of the framed soap composition according to the second embodiment of the present invention, a hydroxy acid ester type surfactant, a monoglyceride type surfactant, a sucrose ester type surfactant or a lactic acid ester type surfactant may preferably be added so that the whipped soap composition poured into the frame may not undergo bubble breakage to cause separation of liquid phase. In particular, it is preferable to add a lactic acid ester type surfactant. Any of these ester type surfactants may preferably be contained in the framed soap composition in an amount of from 1 to 10% by weight, and more preferably from 2 to 5% by weight. If it is in a too small content, the whipped composition tends to undergo bubble breakage, and, if it is in a too large content, the production cost may become higher than the practical level.

To the framed soap compositions according to the first and second embodiments of the present invention, a non-

5 soap type anionic surfactant may preferably be added in order to improve lathering properties at low temperature and dispersion of scum. Such an anionic surfactant may include alkanoyl isethionate, polyoxyethylene ether sulfate, methyl taurate, sarcocinate, sulfosuccinate, monoalkyl phosphate and alkanoyl- $\beta$ -alanine salts, any of which may be used. The non-soap type anionic surfactant may preferably be contained in the framed soap composition in an amount of from 1 to 20% by weight, and more preferably from 5 to 15% by weight. If it is in a too small content or in a too large content, the lathering properties at low temperature and dispersion of scum can not be improved.

10 The framed soap composition of the present invention may also preferably be mixed with a free fatty acid in order to make the soap mild and to improve its lathering properties. As the free fatty acid, hardened coconut oil fatty acid or the like may be used. The free fatty acid may preferably be contained in the framed soap composition in an amount of from 0.2 to 9% by weight, and more preferably from 0.5 to 5% by weight. If it is in a too small content, the soap can not be well made mild and improved in the lathering properties, and, if it is in a too large content, the soap can not lather.

Here, the component-(a) fatty acid soap and the free fatty acid may preferably be contained in a ratio ranging from 99:1 to 85:15, and more preferably 97:3 to 90:10.

15 The framed soap composition of the present invention may also preferably be mixed with an organic acid other than the fatty acids in order to make its fragrance stable. Such an organic acid may include lactic acid and gluconic acid. The organic acid may preferably be contained in the framed soap composition in an amount of from 0.01 to 3% by weight, and more preferably from 0.1 to 1% by weight. If it is in a too small content, it can not be well effective, and, if it is in a too large content, its addition can no longer be expected to be effective enough for its content.

20 Besides the foregoing, when the framed soap composition of the present invention is produced, water must be mixed in order to bring into a uniform molten material the components (a) to (c) and other components optionally added. The water may usually be mixed in an amount of from 25 to 40% by weight. Since the framed soap composition of the present invention rapidly harden after it has been made up, this water is contained in it in substantially the same proportion immediately after its production, but gradually decreases with drying.

25 In addition to the components described above, known additives as used in conventional framed soap compositions may be added to the framed soap composition of the present invention, as exemplified by an antimicrobial agent, a perfume, a pigment, a dye, an oil and other low-irritative agents. Here, the antimicrobial agent may include trichlosan and trichlorocarbanilide, which may usually be mixed in an amount of from 0.1 to 2% by weight. The perfume, pigment or dye may usually be mixed in an amount of from 0.2 to 5% by weight. The oil may include lanolin, paraffin oil, vaseline and isopropyl myristate, which may usually be mixed in an amount of from 0.5 to 5% by weight.

30 The framed soap composition of the present invention can be produced by conventional methods. For example, it can be produced by melting or dissolving the components (a) to (c) and other optional components while heating them to 65 to 80°C with stirring, and pouring the resultant molten material or solution into a frame as it is, followed by cooling and drying.

35 Especially when the light-weight (floating) soap is produced by incorporating air bubbles, it can be produced by subjecting the molten material thus obtained, to aeration treatment using a whipping machine for domestic use or industrial use to incorporate air bubbles, and pouring into a frame the resultant molten material incorporated with air bubbles, followed by cooling to harden and further optionally followed by drying.

#### 40 EXAMPLES

Examples 1 to 5 & Comparative Examples 1 to 4

45 The components formulated as shown in Tables 1 and 2 were melted while heating them at 76°C. The molten materials obtained were each poured into a conventional soap frame without making aeration treatment, and then left to cool to harden. Thus, framed soap compositions were prepared.

Table 1

Components	(wt.%)				
	Example				
	1	2	3	4	5
Sodium laurate	33.3	32.0	15.0	32.2	43.0
Sodium myristate	-	15.0	-	-	-
POE lauryl ether Na sulfate	1.0	0.0	0.0	9.6	11.4
Sodium cocoyl isethionate	2.0	5.0	2.0	-	-
Sodium lauroyl lactylate	4.0	0.0	4.5	-	-
POE monolaurate*1	2.0	2.0	2.5	2.0	2.4
Lactic acid (90%)	-	-	-	0.1	0.1
Lauric acid	0.5	6.0	3.0	4.6	4.5
Myristic acid	-	-	3.0	-	-
Glycerol	17.0	14.6	15.0	9.0	17.6
Sorbitol	3.0	3.5	4.0	4.3	0.0
Sodium chloride	2.0	2.0	1.5	1.0	1.8
Xanthane rubber	-	-	-	0.1	0.0
Perfume	0.6	1.0	1.5	1.1	0.8
Water	34.6	33.9	33.0	25.9	18.5

Remarks:

\*1 The number of EO addition moles of POE monolaurate: 12

Table 2

	Components	(wt.%) Comparative Example			
		1	2	3	4
5					
10	Sodium laurate	42.6	32.1	35.0	40.0
	Sodium myristate	-	-	10.0	-
15	Sodium stearate	-	-	-	20.0
	POE lauryl ether Na sulfate	0.0	8.4	0.0	5.0
	Sodium lauroyl lactylate	-	-	4.0	-
20	POE monolaurate*1	0.0	0.0	2.0	2.0
	Lauric acid	1.6	1.1	3.0	0.0
25	Glycerol	13.8	18.0	15.3	10.0
	Sorbitol	0.0	0.0	0.0	0.0
	Sodium chloride	2.0	2.0	0.0	0.0
30	Perfume	1.0	1.1	1.0	1.0
	Water	39.0	37.3	29.7	22.0
35					

## Remarks:

\*1 The number of EO addition moles of POE monolaurate: 12

## - Evaluation -

With regard to the framed soap compositions of Examples 1 to 5 and Comparative Examples 1 to 4, "hardening rate", "soap hardness after cooling" and "lathering on use" were examined and evaluated in the manner as described below. Results obtained are shown in Table 3.

## Hardening rate:

Neat soap melted at 80 °C was poured into a 30 ml plastic cup (a frame). After making sure of its fluidity, it was left at room temperature for 5 minutes. Thereafter, the framed soap obtained was removed from the frame to visually observe whether or not it deformed when removed. As evaluation criteria, an instance where the molten neat soap was poured into the frame faithfully after its shape and also did not flow or deform after cooling was evaluated as "proper".

Soap hardness after cooling:

According to the vulcanized rubber hardness test method of JIS K6253, a hardness of from 45 degrees to 80 degrees was noted as "sufficient", and 80 degrees or higher, as "hard".

Lathering on use:

Five expert panelists washed their hands to make evaluation. An instance where the soap lathered better than conventional general-purpose milled soaps was indicated as "AA"; an instance where it lathered almost alike, as "A"; an instance where it lathered worse, as "B"; and an instance where it lathered very worse, as "C".

Table 3

Soap hardness			
	Hardening rate	after cooling	Lathering on use
Example:			
1	proper	hard	A
2	proper	sufficient	A
3	proper	sufficient	AA
4	proper	sufficient	AA
5	proper	sufficient	AA
Comparative Example:			
1	low	hard	B
2	low	soft	B
3	hardly fluid	sufficient	B
4	hardly fluid	hard	C

As can be seen from Table 3, the framed soap compositions of Examples 1 to 5 showed superior results in respect of all the "hardening rate", "soap hardness after cooling" and "lathering on use". Also, the framed soap compositions of Examples 1 to 5, thus obtained, were hard to crack and yet hard to become swollen.

On the other hand, in the case of the framed soap compositions of Comparative Examples 1 and 2, in which the component-(b) nonionic surfactant is not contained, they are seen not to be well improved in the hardening rate. In the case of the framed soap compositions of Comparative Examples 3 and 4, in which the component-(c) inorganic salt is not contained, they are seen to be unable to achieve a sufficient fluidity when the molten soap compositions are poured into the frame. Also, the framed soap compositions of Comparative Examples 1 to 4 tended to become swollen. Thus, the framed soap compositions of Comparative Examples 1 to 4 were hard to produce, and were substantially not feasible for commercialization in view of lathering properties and hardness.

#### Example 6 & Comparative Examples 5 to 7

The components formulated as shown in Table 4 were melted while heating them at 80°C. The molten materials obtained were each whipped by batch processing using a domestic whipping machine to make aeration treatment until each came to have a volume of 1.7 times. The material thus whipped was poured into a conventional soap frame, and then left to cool to harden. Thus, framed soap compositions incorporated with air bubbles were prepared.

During the whipping, the temperature dropped by 5 to 8°C, and the temperature at which the molten material was started to harden was about 65°C. To leave 100 ml of the whipped soap composition to cool and harden, it was left for 30 minutes to thereby cool to 40°C or below.

With regard to the framed soap compositions of Example 6 and Comparative Examples 5 to 7, "whipping", "hardening rate", "deformation" and "phase separation" were evaluated in the manner as described below. Results obtained are shown in Table 5.

## Whipping:

The state during aeration treatment was visually observed to judge whether or not the whipping was easy and was possible.

## Hardening rate:

An instance where the molten soap composition did not harden when its temperature was lowered by 10°C while whipping, but hardened in 10 minutes when its temperature was further lowered, was evaluated as "proper". An instance where the molten soap composition did not harden when its temperature was lowered by 10°C while whipping, and finally hardened in 10 minutes when its temperature was further lowered, but was standing over-cooled and did not harden in 10 minutes, was evaluated as "slow hardening". An instance where the molten soap composition hardened up when its temperature was lowered by 10°C while whipping was evaluated as "too rapid hardening".

## Deformation:

Neat soap melted at 80°C was poured into a 30 ml plastic cup (a frame). After making sure of its fluidity, it was left at room temperature for 5 minutes. Thereafter, the framed soap obtained was removed from the frame to visually observe whether or not it deformed when removed. As evaluation criteria, an instance where the molten neat soap was poured into the frame faithfully after its shape and also did not flow or deform after cooling was evaluated as "proper". An instance where the molten neat soap came to have a shape greatly different from the frame when molded, or became greatly holed or became greatly hollow, was evaluated as "deformed". An instance where it did not harden was evaluated as "unconfirmable".

## Phase separation:

An instance where a bubble-free phase was formed at the bottom of the frame to look colored was evaluated as "phase-separated". An instance where a clear separating boundary line was visually recognizable was evaluated as "greatly phase-separated".

Table 4

(wt.%)

Components	Example	Comparative Example		
	6	5	6	7
Sodium laurate	40.0	35.0	30.0	30.0
Sodium myristate	-	10.0	10.0	25.0
POE lauryl ether Na sulfate	1.0	-	-	-
Sodium cocoyl isethionate	1.0	-	2.0	6.0
Sodium lauroyl lactylate	-	4.0	-	4.5
POE monolaurate*1	2.0	2.0	-	2.5
Lauric acid	0.5	3.0	0.5	3.0
Myristic acid	-	-	-	3.0
Glycerol	17.0	15.3	17.0	15.0
Sorbitol	3.0	-	3.0	4.0
Sodium chloride	2.0	-	2.0	1.5
Perfume	0.5	1.0	1.4	1.5
Water	33.0	29.7	34.6	8.0

Remarks:

\*1 The number of EO addition moles of POE monolaurate: 12

Table 5

	Whipping	Hardening rate	Deformation	Phase separation
Example:				
6	easy	proper	none	none
Comparative Example:				
5	difficult	hardened during whipping	none	none
6	difficult	slow	holes of 10 mm deep	greatly phase-separated
7	impossible	proper	unconfirmable	-

As can be seen from Table 5, the framed soap composition of Example 6 showed superior results in respect of all the "whipping", "hardening rate", "deformation" and "phase separation". Also, the framed soap composition of Example 6, thus obtained, was hard to crack and yet hard to become swollen.

On the other hand, in the case of the framed soap composition of Comparative Example 5, in which the component-(c) inorganic salt was not contained, the hardening rate was so high as to make whipping itself difficult, and the molten material hardened up during whipping. Also, the framed soap composition of Comparative Example 6, in which the component-(b) nonionic surfactant was not contained, was difficult to whip and also showed a low hardening rate. It also tended to deform and moreover showed a great phase separation. In the case of the framed soap composition of Example 7, in which the water was in an excessively small content and relatively the component-(a) fatty acid soap was in a large content, bubbles were unstable and consequently the whipping was impossible. Also, the framed soap compositions of Comparative Examples 5 to 7 tended to become swollen and had unpreferable hardness and appearance.

#### Example 7

The relationship between the average bubble size and the swollenness, lathering properties and rubbing solubility of soap was examined using the framed soap composition formulated in Example 3.

More specifically, the components as formulated in Example 3 were melted by heating and mixing them at 75°C. The resultant molten material (flow rate: 19.7 kg/hr), a perfume (flow rate: 0.3 kg/hr) and nitrogen gas (flow rate: 13 NL/hr) were continuously fed to an industrial whipping machine (foaming machine Model MDFO, manufactured by Ebara Seisakusho) to carry out aeration treatment at a number of revolution of 500 rpm, 100 rpm, 75 rpm or 50 rpm. The composition thus obtained was poured into a cup-like container (volume: 100 cc) like the one shown in Fig. 1, which was then put in a -15°C refrigerator for 15 minutes to allow to harden.

After it hardened, the soap incorporated with air bubbles was taken out of the cup-like container, and then cut into two pieces as shown in Fig. 2. Filmy sample A of about 2 cm square was sampled from one cut surface, and cell diameters of 1,000 air bubbles were measured to calculate an average bubble size thereof. Results obtained are shown in Table 6.

With regard to the remaining piece of the soap cut off, rubbing solubility ( $\text{g}/\text{cm}^2$ ) was measured according to JIS K3304 ("Soap Testing Method" 1956). Results obtained are shown in Table 6. Numerical values of the rubbing solubility have the following qualitative meaning.

It means that when the rubbing solubility ( $\text{g}/\text{cm}^2$ ) is less than 4, the solubility is too small; when not less than 4 to less than 7, the solubility is a little small; when not less than 7 to less than 10, the solubility is appropriate; when not less than 10 to less than 14, the solubility is a little great; and when not less than 14, the solubility is too great.

With regard to the other piece of the soap cut off, a swollenness test was made in the manner as described below: The cut surface of the other piece of the soap cut off was immersed in 25°C water for 1 hour, and thereafter taken out to allow it to stand overnight in a desiccator of 100% humidity. The soap was taken out of the desiccator, and a plunger penetration test (JIS K6253 "vulcanized rubber hardness test method") was made on the face immersed in the water to make evaluation as a swollenness test according to the following evaluation criteria. Results obtained are shown in Table 6.

Evaluation criteria:

Rank	Criteria
AA:	Having a sufficient hardness.
A:	Having substantially a sufficient hardness.
B:	Soft, but no problem in practical use.
C:	Soft and flimsy, having a problem in practical use.

Lathering properties were also examined and evaluated in the same manner as in Example 1. Results obtained are shown in Table 6.



Table 6

Evaluation item	Number of revolution of whipping machine			
	500rpm	100rpm	75rpm	50rpm
Average bubble size: ( $\mu\text{m}$ )	58	79	109	125
Rubbing solubility: ( $\text{g}/\text{cm}^2$ )	7.9	10.0	14.5	16.0
Swollenness test:	AA	A	B	B
Lathering properties:	AA	AA	AA	AA

As can be seen from the results of Example 7, the soap tends to become swollen with an increase in the average bubble size. As also can be seen therefrom, a preferable average bubble size is  $80\ \mu\text{m}$  or smaller.

As described above, according to the present invention, a framed soap that may hardly crack and may hardly become swollen can be produced in a productivity comparable to that of the milled soap. Also, a bubble-entrapped soap in which air bubbles are incorporated at a high volume fraction can be readily produced by framing.

#### Claims

1. A framed soap composition comprising the following components (a) to (c):

- (a) from 20 to 50% by weight of a fatty acid soap;
- (b) from 1 to 15% by weight of a nonionic surfactant; and
- (c) from 0.1 to 5% by weight of an inorganic salt.

2. The framed soap composition according to claim 1, wherein the component-(a) fatty acid soap contains a sodium salt of a saturated fatty acid in a proportion of at least 80% by weight.

3. The framed soap composition according to claim 1, wherein the component-(a) fatty acid soap contains lauric acid soap in a proportion of at least 25% by weight.

4. The framed soap composition according to claim 1, wherein the component-(b) nonionic surfactant is a polyoxyethylene fatty acid ester or a polyoxyethylene alkyl ether.

5. The framed soap composition according to claim 1, wherein the component-(b) nonionic surfactant is a compound having as a hydrophilic group a polyoxyethylene group having an average number of ethylene oxide addition moles of from 6 to 150.

6. The framed soap composition according to claim 1, wherein the compound having as a hydrophilic group a polyoxyethylene group having an average number of ethylene oxide addition moles of from 6 to 150 is a compound having as a hydrophobic group an alkyl group having 10 to 18 carbon atoms and is a compound having a value of hydrophilic-lipophilic balance of 8 or more.

7. The framed soap composition according to any one of claims 1 to 6, which is incorporated with air bubbles in a volume fraction of at least 10%.

8. The framed soap composition according to claim 7, which is incorporated with air bubbles in a volume fraction of at least 30%.

9. The framed soap composition according to claim 7, wherein the air bubbles incorporated therein has an average diameter of  $80\ \mu\text{m}$  or smaller.

10. The framed soap composition according to claim 7, which further comprises from 0.2 to 9% by weight of a free fatty acid; said component-(a) fatty acid soap and said free fatty acid being contained in a ratio ranging from 99:1 to 85:15.

11. A process for producing a framed soap composition incorporated with air bubbles, comprising the steps of;

melting a mixture containing the following components (a) to (c):

- 5           (a) from 20 to 50% by weight of a fatty acid soap;  
          (b) from 1 to 15% by weight of a nonionic surfactant; and  
          (c) from 0.1 to 5% by weight of an inorganic salt; while heating the mixture in the presence of water to  
          obtain a molten material;
- 10       subjecting the molten material to aeration treatment to incorporate air bubbles to obtain a molten material  
          incorporated with air bubbles; and  
          pouring the molten material incorporated with air bubbles, into a frame followed by cooling to harden the molten  
          material.

15

20

25

30

35

40

45

50

55

Fig. 1

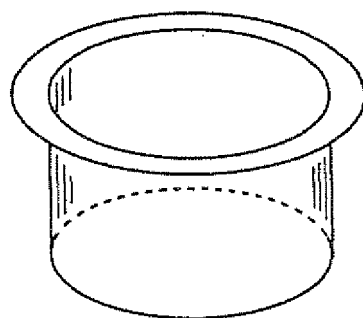
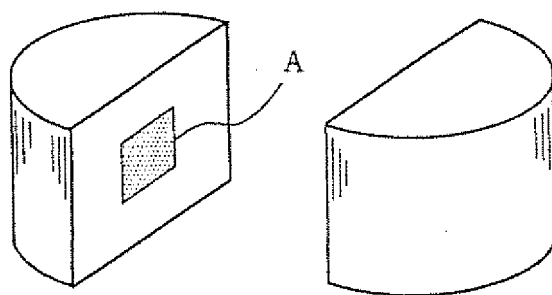
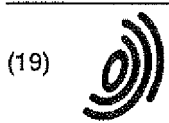


Fig. 2





Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 848 056 A3**

(12)

**EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:  
16.12.1998 Bulletin 1998/51

(51) Int. Cl.<sup>6</sup>: **C11D 10/04**, C11D 17/00  
// C11D1:74, C11D1:72

(43) Date of publication A2:  
17.06.1998 Bulletin 1998/25

(21) Application number: **97121828.4**

(22) Date of filing: **11.12.1997**

(84) Designated Contracting States:  
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE**  
Designated Extension States:  
**AL LT LV MK RO SI**

(30) Priority: **11.12.1996 JP 352215/96**

(71) Applicant: **Kao Corporation**  
**Chuo-Ku Tokyo 103 (JP)**

(72) Inventors:  
• **Eshita, Yoshiyuki**  
**Sumida-ku, Tokyo 131 (JP)**

• **Tonomura, Manabu**  
**Sumida-ku, Tokyo 131 (JP)**  
• **Nozaki, Toshio**  
**Sumida-ku, Tokyo 131 (JP)**  
• **Otani, Hironobu**  
**Sumida-ku, Tokyo 131 (JP)**  
• **Hasegawa, Takeshi**  
**Sumida-ku, Tokyo 131 (JP)**

(74) Representative:  
**Hansen, Bernd, Dr. Dipl.-Chem. et al**  
**Hoffmann Eitle,**  
**Patent- und Rechtsanwälte,**  
**Arabellastrasse 4**  
**81925 München (DE)**

(54) **Framed soap composition**

(57) A framed soap composition comprises (a) from 20 to 50% by weight of a fatty acid soap, (b) from 1 to 15% by weight of a nonionic surfactant, and (c) from 0.1 to 5% by weight of an inorganic salt. A framed soap composition incorporated with air bubbles is produced by melting a mixture containing these components while heating the mixture in the presence of water, subjecting the resultant molten material to aeration treatment to incorporate air bubbles, and pouring the resultant molten material incorporated with air bubbles, into a frame followed by cooling to harden the molten material.

**EP 0 848 056 A3**



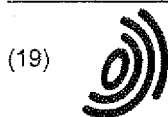
European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 97 12 1828

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO 92 09679 A (PROCTER & GAMBLE) 11 June 1992	1-6, 10, 11	C11D10/04 C11D17/00
Y	* page 1, line 34 - line 36 * * page 12, line 2 - line 9 * * page 15; table 1 * * page 20, line 23 - line 25 * * page 30; table 5 * * page 32; table 6 * * page 38, line 15 - page 39, line 26 *	7-9	//C11D1:74, C11D1:72
Y	US 4 439 355 A (KENKARE) 27 March 1984 * column 3, line 6 - line 21 * * column 7, line 25 - line 51 * * column 8, line 27 - line 32 * * column 9, line 9 - line 12 * * column 10, line 18 - line 63 * * column 11, line 53 - line 60 * * column 14, line 58 - line 61 * * column 15, line 18 - line 27 * & DE 27 53 850 A	7-9	
A	EP 0 617 955 A (KAO) 5 October 1994 * page 3, line 56 - page 4, line 9 * * page 4, line 52 - line 56 * * page 5, line 34 - line 35 *	6	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21 October 1998	Examiner Magrizos, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPC FORM 1503 03 82 (P04C01)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

EP 1 239 027 A1

(12)

**EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 158(3) EPC

(43) Date of publication:

11.09.2002 Bulletin 2002/37

(51) Int Cl.7: **C11D 13/16**

(21) Application number: 01970178.8

(86) International application number:

PCT/JP01/08225

(22) Date of filing: 21.09.2001

(87) International publication number:

WO 02/024858 (28.03.2002 Gazette 2002/12)

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR

(30) Priority: 22.09.2000 JP 2000289621

(71) Applicant: Kao Corporation

Tokyo 103-8210 (JP)

(72) Inventors:

• SHIMADA, Naritoshi  
Tokyo 131-0044 (JP)

• KUNII, Mitsuru  
Tokyo 131-0044 (JP)

• HATANO, Koichi,  
Kao Corporation, Research Lab.  
Haga-gun, Tochigi 321-3426 (JP)

• MIYAMOTO, Yasunori,  
Kao Corporation, Research Lab.  
Haga-gun, Tochi 321-3426 (JP)

• SHIBATA, Manabu,  
Kao Corporation, Research Lab.  
Haga-gun, Tochigi 321-3426 (JP)

• HASEGAWA, Takeshi  
Tokyo 131-0044 (JP)

(74) Representative: HOFFMANN - EITLÉ

Patent- und Rechtsanwälte  
Arabellastrasse 4  
81925 München (DE)

(54) **METHOD OF MANUFACTURING SOAP WITH AIR BUBBLES**

(57) In a method of producing aerated soap (5) comprising solidifying molten soap (4) having a large number of bubbles dispersed therein in a cavity (11) of

a mold (1), the cavity (11) having a prescribed shape, 1.05 or more times as much molten soap (4) as the volume of the aerated soap (5) is fed to the cavity (11) and solidified in a compressed state.

Fig. 3(a)

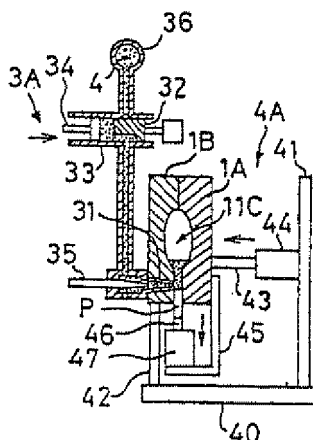


Fig. 3(b)

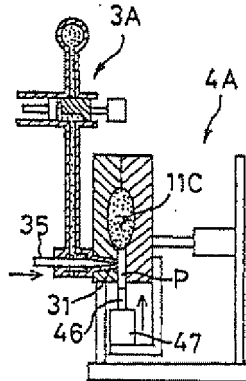


Fig. 3(c)

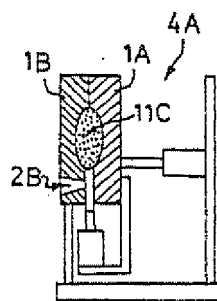
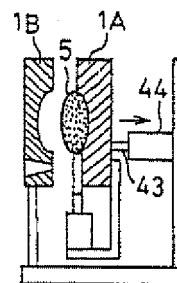


Fig. 3(d)



EP 1 239 027 A1

## Description

### Technical Field:

**[0001]** The present invention relates to a method of producing aerated soap from aerated molten soap. More particularly, it relates to a method of producing aerated soap while preventing shrinkage or development of sink marks on cooling.

### Background Art:

**[0002]** Applicant of the present invention has previously proposed in JP-A-10-195494 a method of producing aerated soap which comprises solidifying molten soap containing a large number of bubbles in a cavity of a mold, wherein the step of solidification is carried out in a hermetically closed cavity. The method aims at preventing development of voids or depressions in solidified soap.

**[0003]** According to this production method, outside air not being allowed to enter the cavity, the solidified soap hardly suffers from void or depression development. However, there still is room for further improvement for preventing soap volume reduction due to contraction of aeration gas on cooling molten soap and for preventing resultant shrinkage and/or development of sink marks.

### Disclosure of the Invention:

**[0004]** Accordingly, an object of the present invention is to provide a method of producing aerated soap while preventing shrinkage and/or sink mark development on cooling in solidifying aerated molten soap.

**[0005]** The present invention accomplishes the above object by providing a method for producing aerated soap which comprises solidifying molten soap having a large number of bubbles dispersed therein in a mold cavity having a prescribed shape, wherein 1.05 or more times as much molten soap as the volume of aerated soap is fed to the cavity and solidified in a compressed state.

### Brief Description of the Drawings:

#### **[0006]**

Fig. 1(a), Fig. 1(b), and Fig. 1(c) are sequential diagrams showing the steps involved in a first embodiment of the method for producing aerated soap according to the invention.

Fig. 2 is a perspective of a mold used in a second embodiment of the method for producing aerated soap according to the invention.

Fig. 3(a), Fig. 3(b), Fig. 3(c) and Fig. 3(d) are sequential diagrams showing the steps involved in the second embodiment of the method for producing aerated soap according to the present invention.

### Best Mode for Carrying out the Invention:

**[0007]** The present invention will be described with reference to its preferred embodiments by referring to the accompanying drawings. Figs. 1(a) to (c) show in sequence the steps involved in the first embodiment of the production method according to the present invention.

**[0008]** As shown in Fig. 1(a), an apparatus used in this embodiment has a mold composed of a lower mold 1 and an upper mold 2 and a feeding section 3. The lower mold 1 is made of a rigid material such as metal and has a cavity 11 facing up. The cavity 11 has a concave shape in conformity to the bottom and sides of an aerated soap as a product. A plurality of interconnecting holes 12 are made in the bottom of the cavity 11 which interconnect the cavity 11 and the outside of the lower mold 1. A clamping mechanism 13 is attached to the sides of the lower mold 1 which clamps the lower mold 1 and the upper mold 2.

**[0009]** The upper mold 2 is also made of a rigid material such as metal. The upper mold 2 is composed of a lid 21, a compressing part 22 which is fitted to the lower side of the lid 21 and the lower side of which is shaped to the upper contour of the aerated soap, a pressing part 23 fitted to the upper side of the lid 21, and a fitting part 24 which is fitted to the pressing part 23 with clearance and engaged with the clamping mechanism 13 of the lower mold 1.

**[0010]** The feeding section 3 has an injection nozzle 31, a switch valve 32, a cylinder 33, and a piston 34 disposed in the cylinder 33. The piston 32 is designed to slide back and forth in the cylinder 33. The volume of molten soap to be fed is decided by the push distance of the piston 34. Molten soap is stored in a storage tank (not shown) and circulating through a circulating duct (not shown) while passing through the storage tank. The flow of the molten soap

is switched by the switch valve to feed the circulating molten soap into the cylinder 33. Separation of the molten soap into gas and liquid is prevented effectively by circulating the molten soap.

[0011] Production of aerated soap by use of an apparatus having the above-described construction will be described. Molten soap having a great number of bubbles dispersed therein is delivered to the cylinder 33 of the feeding section 3. Then, the piston 34 is pushed over a prescribed distance to push out the molten soap, whereby the molten soap 4 is fed to the cavity 11 of the lower mold 1 through the injection nozzle 31. Molten soap having a great number of bubbles dispersed therein can be prepared by, for example, the method described in JP-A-11-43699, filed by the present applicant, col. 2, line 15 to col. 5, line 1.

[0012] Various gases are useful for aerating molten soap. In particular, an inert gas, especially a non-oxidizing inert gas such as nitrogen gas, is effective to prevent the molten soap components from being oxidatively decomposed on heating to generate offensive odors, etc.

[0013] The molten soap is fed into the cavity 11 in an amount at least 1.05 time, preferably 1.1 or more time, still preferably 1.15 or more time, as much as a target volume as an aerated soap. Shrinkage and sink mark development due to cooling of the molten soap can be effectively prevented by feeding the recited volume of molten soap, assisted by the compression of the molten soap as described later. It is predictable that shrinkage or sink mark formation on cooling would hardly occur where a larger amount of molten soap than a set volume of an aerated soap is fed and compressed. The characteristic of the present invention resides in the finding that such an unpredictably small excess of volume, i.e., 1.05 or more time as much as the set volume of an aerated soap suffices to effectively prevent shrinkage or sink mark development on cooling. The upper limit of the molten soap volume to be fed is decided appropriately according to the volumetric proportion of bubbles present in the molten soap. For example, molten soap containing a relatively large proportion of bubbles will shrink to a larger degree on cooling so that the upper limit of the volume to be fed will be raised. On the other hand, where molten soap has a relatively small proportion of bubbles, the upper limit of the volume to be fed is relatively small because the degree of shrinkage on cooling will not be so high. Taking into consideration that the total volume of bubbles in the molten soap according to this embodiment is about 5 to 70%, a preferred upper limit of the volume to be fed is three times, particularly two times, the volume of aerated soap. The upper limit of the volume to be fed being three times, particularly two times, the volume of aerated soap is also preferred for preventing soap from losing its shape during the production or use on account of loss of hardness.

[0014] The volume of molten soap varies with pressure and temperature. The term "volume of molten soap" as used herein means the volume at 25°C under atmospheric pressure.

[0015] It is preferred that the molten soap be maintained at a temperature of 55 to 80°C, particularly 60 to 70°C, when fed to the cavity 11 to prevent the molten soap from solidifying at the tip of the injection nozzle while preventing oxidation of soap and deterioration of perfume.

[0016] In this connection, the molten soap is preferably injected into the cavity 11 at a temperature higher than the melting point by 1 to 20°C, particularly 2 to 5°C, for the same reason.

[0017] It is preferred for the molten soap injected into the cavity 11 to have a viscosity of 0.001 to 50 Pa·s, particularly 0.01 to 10 Pa·s, especially 0.02 to 5 Pa·s. At a viscosity above the upper limit, injecting molten soap into the cavity 11 is difficult and needs a pump with greater output, which makes the production equipment larger. The lower limit of the viscosity practically depends on the viscosity of water contained in the molten soap. The viscosity of molten soap is measured as follows. Molten soap is poured in a cylindrical tube having an inner diameter of 10 mm and a length of 1880 mm with its downstream end open. The other end (upstream end) of the tube is provided with a pressure gage. The pressure at a shear rate of 300<sup>-1</sup> is read, and the melt viscosity is calculated from the reading according to Hagen-Poiseuille equation. Hagen-Poiseuille equation is described, e.g., in Micheal R. Lindeburg, *Engineering Training Reference Manual* 8th Ed., pp. 17-5 to 17-6, Professional Publications, Inc., Belmont, CA, which is incorporated herein by reference. The measuring temperature is the same as the temperature of the molten soap actually injected into the cavity.

[0018] Upon completion of feeding the molten soap 4, the upper side of the lower mold 1 is closed with the upper mold 2, and the fitting part 24 fitted to the upper mold 2 is engaged by the clamping mechanism 13 attached to the lower mold 1. Thus, the two molds are fixed. Then, as shown in Fig. 1(b), the pressing part fitted to the upper mold 2 is pressed down by a prescribed pressing means (not shown), such as a pressure cylinder, to compress the molten soap 4 in the cavity 11 to a set volume of an aerated soap as a product. The molten soap is let to solidify in this compressed state. These operations effectively prevent development of shrinkage and sink marks on cooling the molten soap to provide cakes of aerated soap with satisfactory appearance.

[0019] The pressure (gauge pressure) for compressing the molten soap is usually about 0.005 to 0.3 MPa, particularly about 0.05 to 0.2 MPa, while varying according to how many times as much as the set volume of an aerated soap the fed molten soap volume is.

[0020] The compression ratio of the molten soap, i.e., the compression ratio of the gaseous components in the molten soap (volume of gaseous components before compression/volume of gaseous components after compression) is preferably 1.08 to 2.5, still preferably 1.1 to 2, from the standpoint of preventing development of shrinkage or sink marks



on cooling, reducing the cooling time, and improving productivity. The gaseous components in the molten soap include the gas used for aerating molten soap, steam contained in molten soap, and the like.

[0021] The solidification time of the molten soap can be shortened by cooling the lower mold 1 by a prescribed means, for example, a coolant such as water. As a matter of course, spontaneous cooling will do. Where the mold is cooled with water, the water temperature is preferably about 5 to 25°C for preventing non-uniform dispersion of bubbles on cooling.

[0022] The molten soap is preferably solidified so that the resulting aerated soap may have an apparent density of 0.4 to 0.85 g/cm<sup>3</sup>, particularly 0.6 to 0.8 g/cm<sup>3</sup>. This is preferred for securing the fluidity of the molten soap, improving the cooling efficiency, improving releasability of aerated soap from the cavity 11, and improving appearance of the resulting soap. Such a solidified state can be achieved by, for example, feeding aerated molten soap made of 55 ml (under atmospheric pressure) of nitrogen gas and 90 ml of a soap composition into the cavity 11 at 64°C, compressing the aerated molten soap to 120 ml, and letting the molten soap to solidify in this compressed state. The method of measuring the apparent density of aerated soap will be described in Examples hereinafter given.

[0023] It is also preferred that the molten soap is solidified in such a manner that the proportion of bubbles (pores) having a size of 1 to 300 μm in the total pore volume in the resulting aerated soap (hereinafter referred to as a pore volume fraction) may be 80% or more for improving latherability and preventing the soap from getting sodden or swollen in contact with water. Such a solidified state can be obtained by aerating a soap composition by means of, for example, an aeration apparatus Euromix MDFO supplied by Ebara Corp. at a rotor's rotation speed of 1000 kPa (500 rpm), and solidifying the aerated molten soap in the cavity by cooling while keeping the molten soap in a compressed state. The method of measuring the pore volume fraction of aerated soap will be described in Examples hereinafter given.

[0024] On completion of solidification of the molten soap, the engagement of the clamping mechanism 13 attached to the lower mold 1 and the fitting part 24 attached to the upper mold 2 is released, and the upper mold 2 is removed as shown in Fig. 1(c). The aerated soap 5 is taken out of the cavity 11 of the lower mold 1 by using a prescribed holding means, for example, a vacuum gripper. To facilitate removal of the aerated soap from the mold, gas such as air may be blown into the cavity 11 through the interconnecting holes 12 made in the bottom of the cavity 11.

[0025] The aerated soap thus obtained assumes a satisfactory outer appearance with neither shrinkage nor sink marks which may have developed on cooling the molten soap. Further, the bubbles inside the aerated soap are spherical. Having spherical bubbles, the soap exhibits moderate water repellency, adding improvement on conventional aerated soap having the demerit of easily getting sodden or swollen in contact with water.

[0026] Compounding components which can make up the aerated soap include fatty acid soaps, nonionic surface active agents, inorganic salts, polyols, non-soap type anionic surface active agents, free fatty acids, perfumes, and water. If desired, such additives as antimicrobials, pigments, dyes, oils, and plant extracts, can be added appropriately. The second embodiment of the present invention will then be described by referring to Figs. 2 and 3. The second embodiment will be described only with reference to differences from the first one. With reference to the particulars that are not described hereunder, the description on the first embodiment applies appropriately. In Figs. 2 and 3 the same members as in Fig. 1 are given the same numerals used in Fig. 1.

[0027] The mold shown in Fig. 2 is a split mold made of a pair of split pieces, a first piece 1A and a second piece 1B. Each piece is made of a rigid material such as metal and has a rectangular block shape with a depression 11A or 11B in its central portion. The depressions 11A and 11B are shaped to provide a cavity (not shown) in agreement with the contour of a soap to be produced when the first piece 1A and the second piece 1B are joined together on their parting faces PL.

[0028] The second piece 1B has a nozzle insert hole 2B piercing through the outer periphery around the depression 11B in the thickness direction. The diameter of the nozzle insert hole 2B increases gradually toward the back side of the second piece 1B. The first piece 1A has a gate 2A of semicircular section engraved on part of its parting face PL. The gate 2A connects the edge side E and the depression 11A of the first piece 1A. A piston P mating the shape of the gate 2A is inserted in the gate 2A. The piston P is made of metal, plastic, etc. and designed to slide in the gate 2A. The nozzle insert hole 2B and the gate 2A are made in the respective pieces in such a configuration as to provide a tunnel connecting the nozzle insert hole 2B, the gate 2A, and the cavity when the first piece 1A and the second piece 1B are joined together on their parting faces PL. While not shown, an air vent is provided on the parting face PL of the second piece 1B. While not shown, a passageway for cooling water circulation is made in the blocks constituting the pieces 1A and 1B.

[0029] Loops L of a buckle mechanism are attached to both sides of the first piece 1A, and hooks F of the buckle mechanism are attached to both sides of the second piece 1B. The loops L and the hooks F are positioned so that they are engaged with each other with the first and the second pieces 1A and 1B joined on their parting faces PL.

[0030] The mold shown in Fig. 2 is used as fitted to the production apparatus shown in Fig. 3. The production apparatus has a mold unit 4A and a molten soap injection unit 3A. The mold is fitted above a base plate 40 of the mold unit 4A as shown in Fig. 3(a). The base plate 40 has an upright support plate 41 for the first piece 1A and an upright support plate 42 for the second piece 1B. The support plate 41 has fixed to the inner side thereof a cylinder 44 having a piston

43. The cylinder 44 is fixed so that the piston 43 may slide in the direction perpendicular to the support plate 41. The tip of the piston 43 is fixed to the back of the first piece 1A. Accordingly, the first piece 1A is a horizontally movable half of the mold. The first piece 1A is fitted with its gate 2A side down. An L-shaped cylinder holding member 45 is attached to the lower part of the back of the first piece 1A. The horizontal part of the cylinder holding member 45 has a cylinder 47 with a piston 46. The cylinder 47 is fitted to allow the piston 46 to slide vertically. The tip of the piston 46 is connected to the piston P disposed in the first piece 1A.

[0031] The second piece 1B is fitted to the support plate 42 with its nozzle insert hole 2B down and its depression 11B facing the depression 11A of the first piece 1A. As is understood from Fig. 3(a), the second piece 1B is a fixed half of the mold. The molten soap injection unit 3A is provided in the rear of the second piece 1B. The injection unit 3A comprises an injection nozzle 31, a switch valve 32, a cylinder 33, and a piston 34 disposed in the cylinder 33. The injection nozzle 31, being shaped in conformity with the shape of the nozzle insert hole 2B made in the second piece 1B, is inserted in the nozzle insert hole 2B. A gate pin 35 is provided to slide inside the injection nozzle 31. The injection of molten resin through the injection nozzle 31 to the cavity is controlled through push and pull of the gate pin 35. The switch valve 32 serves to connect the cylinder 33 to either a circulating duct 36 which passes through a storage tank (not shown) or the injection nozzle 31. In the state shown in Fig. 3(a), the cylinder 33 connects to the injection nozzle 31, with the connection between the cylinder 33 and the circulating duct 36 shut off.

[0032] The method of producing aerated soap by use of the production apparatus shown in Fig. 3 is described below. The cylinder 44 of the mold unit 4A operates to push the piston 43 forward to join the first piece 1A and the second piece 1B to close the split mold. The buckie mechanism (see Fig. 2) is fastened to clamp the split mold. Water is made to circulate through the above-mentioned cooling water passageway made in both split mold pieces. The cylinder 47 operates to draw back the piston 46, whereby part of the piston P connected to the piston 46 is drawn out of the first piece 1A. In the injection unit 3A, on the other hand, while the piston 34 is in a pushed state, the switch valve 32 operates to connect the cylinder 33 to the circulating duct 36. The piston 34 is then drawn back to deliver a predetermined amount of molten soap into the cylinder 33. The switch valve 32 then operates to cut the connection between the cylinder 33 and the circulating duct 36 and connect the cylinder 33 to the injection nozzle 31 as shown in Fig. 3(a). Subsequently, the piston 34 is pushed to push the molten soap 4 out of the cylinder 33. It follows that the molten soap 4 is injected under pressure into the cavity 11C through the injection nozzle 31 and the gate 2A (see Fig. 2). Similarly to the first embodiment, the volume of the molten soap to be injected is at least 1.05 time the target volume of an aerated soap. This expression does not mean that a greater amount than 1.05 time is preferred as is preferred in the first embodiment. In other words, 1.05 or more time as much molten soap as the target volume is enough. The molten soap in the cavity 11C is compressed to a set volume of an aerated soap by this operation of injection under pressure. Unlike the first embodiment, the present embodiment does not require separation of a compression step from the molten soap feeding step. That is, compression of molten soap is effected in the feeding step. Accordingly, the production method of the second embodiment achieves an increased production efficiency over that of the first embodiment. Besides, the production apparatus used in the second embodiment involves a shorter stroke in the machine movement than that used in the first embodiment, furnishing another merit that the size of the apparatus can be reduced.

[0033] Upon completion of injecting a prescribed volume of molten soap under pressure, the gate pin 35 is pushed to shut off the connection between the injection nozzle 31 and the cavity 11C as shown in Fig. 3(b). The cylinder 47 then operates to push the piston 46 thereby pushing the piston P connected to the piston 46 into the gate 2A (see Fig. 2). As a result, the molten soap remaining in the gate 2A is injected into the cavity 11C.

[0034] The mold unit 4A is then withdrawn (moved to the right in the drawing) whereby the injection unit 3A is separated from the second piece 1B as shown in Fig. 3(c), and the molten soap in the cavity 11C is cooled and solidified in the compressed state. As previously stated, the pieces 1A and 1B have been cooled to a prescribed temperature by the circulating cooling water to accelerate the cooling solidification of the molten soap in the cavity 11C. Since the molten soap has been injected under pressure in a volume 1.05 or more time the set volume of an aerated soap and compressed, shrinkage and sink mark development on cooling solidification of the molten soap are prevented.

[0035] On solidifying the molten soap, the engagement of the buckle mechanism which has been fixing the split mold pieces 1A and 1B is relieved. The cylinder 44 operates to draw back the piston 43 to separate the pieces 1A and 1B as shown in Fig. 3(d). The aerated soap 5 is then taken out of the cavity by a prescribed holding means (not shown).

[0036] The present invention is by no means limited to the above-described embodiments. For example, while in the first embodiment aerated soaps are produced by the use of the lower mold 1 and the upper mold 2, the lower mold 1 may be composed of a plurality of pieces according to the contour of a desired aerated soap product.

[0037] The mold used in the first and the second embodiments may be replaced with a hollow member made of a synthetic resin such as polyethylene, polypropylene, polycarbonate or polyester; a flexible thin metal plate; a flexible rubber material, etc. Such a hollow member may be used as inserted in the mold used in the second embodiment, and molten soap is fed into the hollow member and solidified in a compressed state. In this case, there is an advantage that the hollow member serves as a packaging container of the resulting aerated soap.

## EXAMPLES 1 TO 4 AND COMPARATIVE EXAMPLE 1

[0038] Molten soap having a great number of bubbles dispersed therein was prepared from the compounding components shown in Table 1 below in accordance with the method described in JP-A-11-43699 *supra*. Nitrogen gas was used for aeration.

TABLE 1

Compounding Component of Molten Soap	Part by Weight
sodium laurate	30.0
sodium cocoyl isetionate	2.0
sodium lauroyl lactate	5.0
polyoxyethylene monolaurate	2.0
lauric acid	5.0
glycerol	20.0
sodium chloride	1.5
perfume	1.5
water	32.0

[0039] Aerated soaps were produced from the prepared molten soap according to the steps shown in Figs. 1(a) through (c). The molten soap was fed to the cavity 11 of the lower mold 2. The temperature and the injected volume of the molten soap were as shown in Table 2. The upper side of the lower mold 1 was closed with the upper mold 2, and the molten soap was compressed to a set volume (120 cm<sup>3</sup>) by the compressing part 22 of the upper mold 2. The compression ratio of the molten soap was as shown in Table 2. In this compressed state the lower mold was cooled with cooling water at 5 to 15°C for 3 to 15 minutes to solidify the molten soap.

[0040] On completion of solidification of the molten soap, the upper mold 2 was removed. The aerated soap was taken out of the cavity 11 by means of a vacuum gripper while blowing compressed air into the cavity 11 through the interconnecting holes 12 made through the bottom of the cavity 11. There was thus obtained an aerated soap as a final product.

[0041] The apparent density and the pore volume fraction of the resulting aerated soap were measured according to the following methods. The outer appearance of the soap was evaluated based on the following standard. The results obtained are shown in Table 2.

## Measurement of apparent density

[0042] A rectangular parallelepiped specimen having known side lengths (e.g., 10 to 50 mm) was cut out of the resulting aerated soap and weighed. The weight was divided by the volume to give the apparent density. The volume was calculated from the three side lengths. The weight measurement was made with an electron balance. The measurement was made at 25°C±3°C and a relative humidity of 40 to 70%.

## Measurement of pore volume fraction

[0043] An aerated soap was rapidly cooled to -196°C and cut at -150°C. The cut surface was observed in vacuo at -150°C under an electron microscope Crio SEM JSM-5410/CRU, manufactured by JEOL Hightech Co., Ltd. The accelerating voltage was 2 kV, and a secondary electron image was used as detection signals. The diameter of pores was measured on a micrograph (magnification 500X), and a pore volume fraction was calculated from the measured diameter.

## Evaluation of appearance

[0044] The appearance was observed with the naked eye and graded according to the following standard.

A ... Equal to the cavity shape

B ... Substantially equal to the cavity shape

C ... Sink marks were observed as compared with the cavity shape.

TABLE 2

		Example				Comparative Example
		1	2	3	4	1
Molten Soap	Injected Volume (%*)	118	125	112	135	100
	Temp. (°C)	64	65	55	70	50
	Compression Ratio	1.49	1.64	1.45	1.86	1.0
Aerated Soap	Apparent Density (g/cm <sup>3</sup> )	0.64	0.62	0.75	0.6	0.85
	Pore Volume Fraction (%)	100	100	100	100	100
	Appearance	A	A	B	B	C

Note: \* Based on a set volume of an aerated soap

[0045] As is obvious from the results shown in Table 2, the aerated soaps obtained in Examples exhibit satisfactory appearance with neither shrinkage nor sink marks due to cooling. While not shown in the Table, the aerated soaps obtained in Examples gave off no offensive odor attributed to heating of the molten soap. To the contrary, the aerated soaps of Comparative Example showed partial missing or sink marks ascribed to cooling.

#### EXAMPLES 5 TO 7 AND COMPARATIVE EXAMPLE 2

[0046] Molten soap having a large number of bubbles dispersed therein was prepared from the same compounding components as used in Example 1 in accordance with the same procedure as in Example 1. Aerated soaps were produced from the prepared molten soap by use of the mold shown in Fig. 2 according to the steps shown in Figs. 3 (a) through (d). The temperature and the injected volume of the molten soap were as shown in Table 3. Each split mold pieces had been cooled with cooling water at 5 to 15°C. The molten soap cooling time was 3 to 15 minutes. Otherwise, the same procedures as in Example 1 were followed to obtain aerated soaps. The apparent density and the pore volume fraction of the resulting aerated soaps were measured, and the appearance of the soaps was evaluated in the same manner as in Example 1. The results obtained are shown in Table 3.

TABLE 3

		Example			Comparative Example 2
		5	6	7	
Molten Soap	Injected Volume (%*)	110	106	116	100
	Temp. (°C)	64	64	64	64
	Compression Ratio	1.41	1.22	1.59	0.99
Aerated Soap	Apparent Density (g/cm <sup>3</sup> )	0.78	0.75	0.76	0.71
	Pore Volume Fraction (%)	100	100	100	100
	Appearance	A	A	A	C

Note: \* Based on a set volume of an aerated soap

[0047] As is apparent from the results shown in Table 3, the aerated soaps obtained in Examples exhibit satisfactory appearance with neither shrinkage nor sink marks due to cooling. While not shown in the Table, the aerated soaps obtained in Examples gave off no offensive odor attributed to heating of the molten soap. To the contrary, the aerated soaps of Comparative Example showed partial missing or sink marks ascribed to cooling. In particular as is apparent from comparison between Example 7 and Comparative Example 2, it is clearly understood that shrinkage and sink mark development on cooling can be prevented by feeding and compressing 1.05 or more time as much molten soap as the volume of the aerated soap in the cavity.

Industrial Applicability:

[0048] According to the method of the present invention for producing aerated soap, aerated molten soap can be solidified while effectively preventing shrinkage and/or sink mark development on cooling.

[0049] In particular, use of an inert gas for aerating molten soap effectively prevents generation of offensive odors attributed to heating of the molten soap.

Claims

1. A method for producing aerated soap which comprises solidifying molten soap having a large number of bubbles dispersed therein in a mold cavity having a prescribed shape, wherein 1.05 or more time as much molten soap as the volume of the aerated soap is fed to said cavity and solidified in a compressed state.
2. The method for producing aerated soap according to claim 1, wherein 1.05 or more time as much molten soap as the volume of the aerated soap is injected into said cavity under pressure, and said molten soap in said cavity is compressed to the volume of the aerated soap by said injection under pressure and solidified in the compressed state.
3. The method for producing aerated soap according to claim 1, wherein 1.05 or more time as much molten soap as the volume of the aerated soap is fed to said cavity, and said molten soap in said cavity is compressed to the volume of the aerated soap by a prescribed compressing means and solidified in the compressed state.
4. The method for producing aerated soap according to claim 1, wherein said molten soap is molten soap having been aerated with an inert gas.
5. The method for producing aerated soap according to claim 1, wherein said molten soap is injected into said cavity at a temperature of 55 to 80°C.
6. The method for producing aerated soap according to claim 1, wherein said molten soap is solidified to provide aerated soap having an apparent density of 0.4 to 0.85 g/cm<sup>3</sup>.
7. The method for producing aerated soap according to claim 1, wherein said molten soap is solidified to provide aerated soap containing bubbles having a size of 1 to 300 μm in a proportion of 80% or more in the total volume of bubbles.

Fig. 1(a)

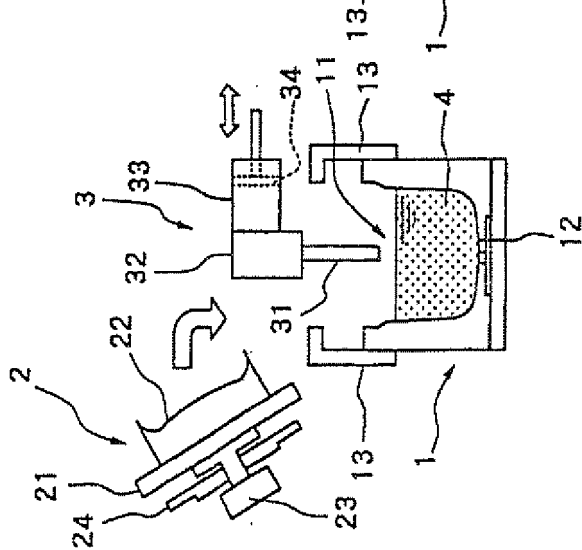


Fig. 1(b)

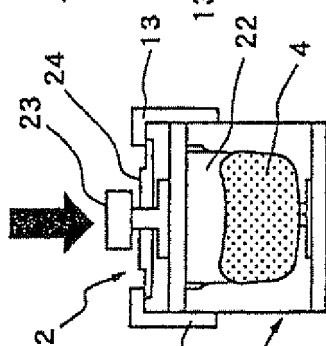


Fig. 1(c)

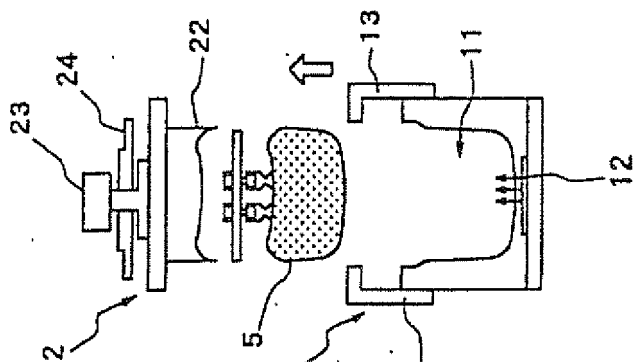


Fig. 2

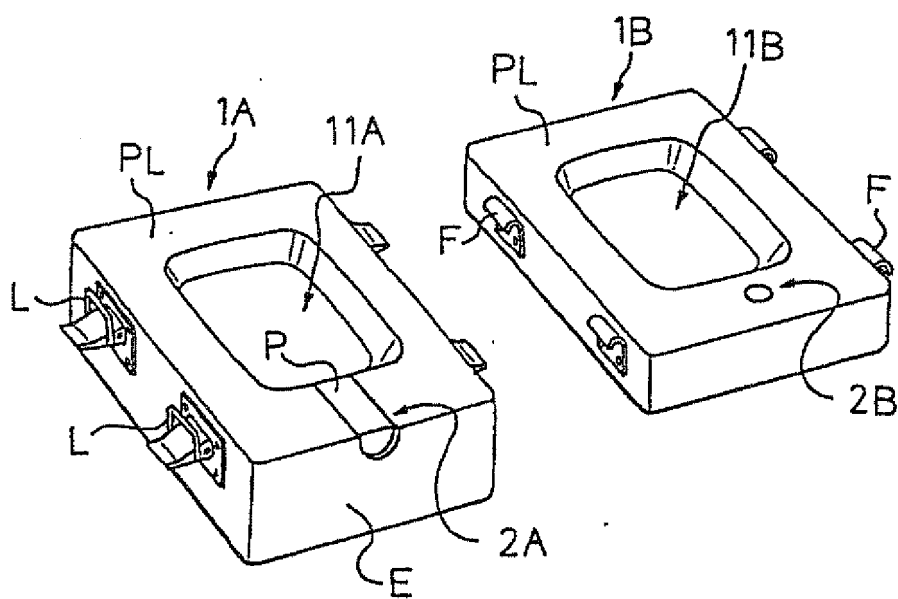


Fig. 3(a)

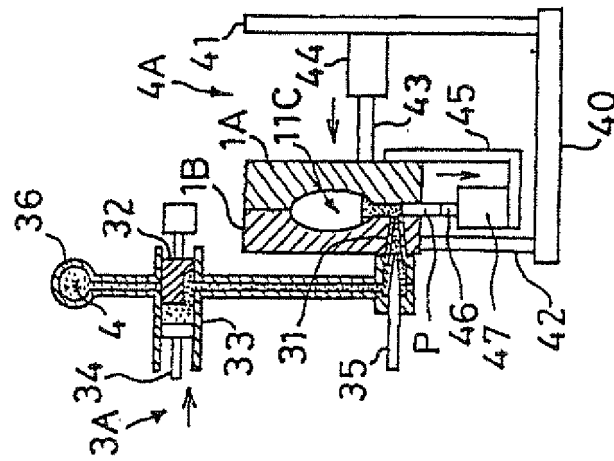


Fig. 3(b)

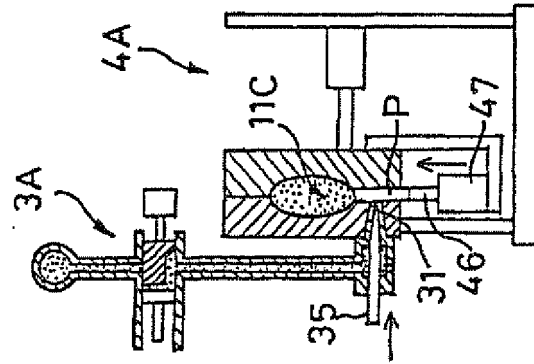


Fig. 3(c)

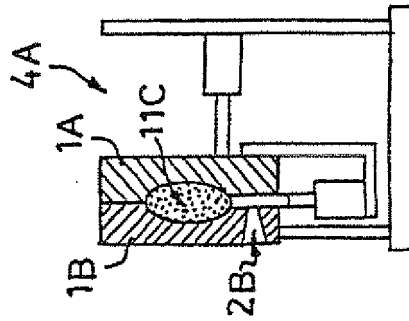
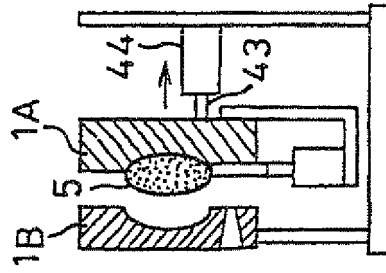


Fig. 3(d)





## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/08225

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. <sup>7</sup> C11D 13/16		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. <sup>7</sup> C11D 1/00-C11D 19/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 10-195494 A (Kao Corporation), 28 July, 1998 (28.07.98), abstract; Claims; drawings; Cited in the present application (Family: none)	1-7
A	JP 11-43699 A (Kao Corporation), 16 February, 1999 (16.02.99), abstract; Claims; drawings; Cited in the present application (Family: none)	1-7
A	JP 10-195495 A (Kao Corporation), 28 July, 1998 (28.07.98), abstract; Claims; drawings (Family: none)	1-7
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
Date of the actual completion of the international search 12 December, 2001 (12.12.01)		Date of mailing of the international search report 25 December, 2001 (25.12.01)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/08225

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 4-218599 A (Colgate-Palmolive Company), 10 August, 1992 (10.08.92), abstract; Claims & CA 2037310 A            & HU 57825 A & CS 9100548 A            & BR 9100796 A & CN 1057481 A            & ZA 9101267 A & RO 106758 A            & EG 19135 A & PL 166591 B            & RU 2039084 A & BG 60595 B	1-7
A	US 3149188 A (Paul Schmitt), 15 September, 1964 (15.09.64), Claims; drawings & DE 1149846 A	1-7

Form PCT/ISA/210 (continuation of second sheet) (July 1992)



(18)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 413 284 A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 90115493.0

(51) Int. Cl.<sup>5</sup>: **C11D 9/00, C11D 9/04,  
C11D 9/06, C11D 9/26,  
C11D 9/44**

(22) Date of filing: 13.08.90

(30) Priority: 15.08.89 US 393934

(43) Date of publication of application:  
20.02.91 Bulletin 91/08

(84) Designated Contracting States:  
**AT BE CH DE DK ES FR GB IT LI LU NL SE**

(71) Applicant: **Colgate-Palmolive Company**  
**300 Park Avenue**  
**New York, N.Y. 10022-7499(US)**

(72) Inventor: **Colwell, Dennis J.**  
**One Cornwall Drive**  
**East Windsor, N.J.(US)**  
Inventor: **Pflug, James J.**  
**19 Roanoke Court**  
**Bordentown, N.J.(US)**

(74) Representative: **UEXKÜLL & STOLBERG**  
**Patentanwälte**  
**Beselerstrasse 4**  
**D-2000 Hamburg 52(DE)**

(54) **Bar soap having improved resistance to cracking.**

(57) A bar soap prepared from a tallow-coco soap chip base containing minor amounts of filler, dye and water and from 1 to 5 percent long chain primary alcohol, to reduce or eliminate wet cracking of the bar during use.

**EP 0 413 284 A2**

## BAR SOAP HAVING IMPROVED RESISTANCE TO CRACKING

FIELD OF THE INVENTION

The present invention relates to a novel bar soap prepared from 60 to 85 percent tallow, 15 to 40 coco soap chip and 1.5-5% saturated long chain primary alcohol having from 16-18 carbon atoms in the molecule characterized by resistance to wet cracking during use.

BACKGROUND OF THE INVENTION

The tendency of bar soap to form cracks when repeatedly moistened and dried during use is well known. This disturbing characteristic is particularly evident and bars containing a coloring agent. This tendency is undesirable in that it wastes soap and also gives a soap an unpleasant appearance during use. When bar soap is subjected to several cycles of washing and drying out it has a tendency to develop edge and face cracks. The soap color tends to bleed thus giving the soap an unpleasant appearance during use.

It has been found that addition of a straight chain primary alcohol which has 16-18 carbon atoms in the molecule, to a bar soap such as the 85% tallow 15% coco chip bar, containing a coloring agent, titanium oxide and water greatly reduces the tendency of the bar to crack during continuous cycle of wetting and drying out.

U.S. Patent 4,014,807 to Werner et al describes washing agent based on synthetic detergents containing 1 to 10% branched chained alkanols in combination with di-octyl adipate. The product is characterized by a resistance to cracking during use.

U.S. Patent 4,477,363 to Wong et al describes a buffered alkali earth metal surfactant bar containing 1-15% fatty alcohol that exhibits improved longevity and improved stability.

U.S. Patent 3,186,948 to Sweeney describes detergent toilet bars that use polyhydric alcohols as binders in the soap formulation.

U.S. Patent 3,766,097 to Rosmarin describes a composition useful for the manufacture of a detergent that contains from 5-15% of the polyhydric alcohol and beeswax.

U.S. Patent 4,547,307 to Hoppe et al describes bar soap with deodorizing action in which one of the components is wood wax alcohol.

U.S. Patent 4,234,484 to Morshauser describes a detergent bar containing a fatty alcohol as a binder.

SUMMARY OF THE INVENTION

It has been found that a bar soap based on 60 to 85 percent tallow 15 to 40 percent coco soap chip containing a coloring agent, titanium dioxide and sufficient water to provide about 10% water in the final product can be made resistant to cracking during wetting, drying and rewetting cycles by adding 1-5% of a long chain primary alcohol, having 16-18 carbon atoms in the molecule, to the formulation.

Accordingly it is a primary object of the present invention to prepare a bar soap based on 60 to 85 percent tallow 15 to 40 percent coco soap chip which eliminates or substantially reduces the wet cracking tendency of the bar.

Another object of the invention that it provides bar soap based on 60 to 85 percent tallow 15 to 40 percent coco soap chip containing a dye and titanium dioxide which exhibits elimination or improvement in the cracking and coloring bleeding tendencies of the soap bar.

DETAILED DESCRIPTION OF THE INVENTION

Bar soaps, such as those based on tallow and coco soap chip are well known. The instant invention resides in the discovery that the addition of saturated long chain (16 to 18 carbon atoms in the molecule) primary alcohols to the formulation greatly reduces or eliminates wet cracking in the bar soap. The most

important features of a long chain primary alcohol are 1. Single hydrogen bonding site per molecule. 2. Minimal solubility in water and 3. Saturated hydrocarbon chain. The preferred primary alcohol is stearyl alcohol Cetyl(1-hexadecanol) can be substituted for the stearyl alcohol in the formulation. Examples of other suitable alcohols include myristyl(1-tetradecanol).

5 The present invention is an improvement over the prior art in that the process is simple and does not require new equipment and that a number of functional benefits can be achieved including improvement in reduction of cracking and color bleeding when the bars are used for some time and subjected to cycles of wetting drying and rewetting.

The first step in the process of preparing the bar is the selection of the base. The base containing 85% tallow and 15% coco soap chip is preferred however other conventional combinations of the ingredients that are used for bar soap manufacturer such as for example, 60% tallow and 40% coco soap chip can also be used. The bar soap formulation also contains from about 0.01 to 1.0% preferably 0.5% titanium dioxide 0.01 to 1.0% preferably 0.25 % of a dye solution to impart color to the soap and 5.0 to 12.0% water in the final bar.

15 The long chain primary alcohols are added to the formulation containing the other ingredients. The other steps in the process are conventional. The ingredients are milled by three passes through a mill. In the first pass the water is added to break up the chip. The color, titanium dioxide and the long chain alcohol components are added in the second pass. The third pass insures the composition will be uniform.

The next step of the process the milled mixture is plodded. Any conventional plodder equipment can be used. A four inch plodder was used to allow for a larger batch and less finished soap variability. The mixture was plodded twice and extruded as a billet at a temperature of 100° F. The billets were formed in the extrusion step and cut to the desired length, and pressed into bar shape .

The invention is illustrated by the following specific but nonlimiting examples.

25

#### EXAMPLE 1

In this example a formulation was prepared to contain 89.64% of the 85% tallow 15% coco soap chip formulation. The soap chip was transferred to a mill and sufficient water was added in the first pass through to break up the chip to provide 10% moisture in the final product. The other ingredients, 0.28% color solution 0.08% titanium oxide and 5% stearyl alcohol were added after the stearyl alcohol was heated to 140-145° F. The ingredients were mixed in the third pass in the mill to insure uniformity composition. The milled product was plodded in a four inch plodder to allow for larger batch and less finished soap variability. The plodded mixture was extruded at a temperature of a 100° F and that the soap was cut into bars of the desired size and shape.

35

#### EXAMPLE 2

40 A control formulation was prepared identical to the formulation in example 1 except that no stearyl alcohol was added. The 85% tallow 15% coco soap chip component was 94.64% of the formulation. The water, titanium oxide and color solution were added using the techniques described in Example 1. The mixture was milled, plodded and extruded using technique as described in example 1.

45

#### EXAMPLE 3

The cracking properties of the product were evaluated by partially immersing bars in water at 70°F for four hours then allowing the bars to air-dry in a temperature and humidity controlled room, for 24 hours. The samples were then rated for edge and face cracks on a 0-5 scale, 0 representing no cracking. A total of 23 control bars prepared according to the method of example 2 and 28 stearyl alcohol prototypes prepared according to the method described in Example 1 were evaluated. A statistical analysis of the test results performed using the function of RSI, to establish validity of test. The following results were obtained.

55

TABLE 1

TWO SAMPLE COMPARISONS	
Control vs. Stearyl/Edge Cracks	p < .05
Control vs. Stearyl/Face Cracks	p < .05

The mean values and standard deviations are set out in Table 2

TABLE 2

MEAN VALUES AND STANDARD DEVIATIONS		
	$\bar{X}$	SD
Stearyl Edge Cracks	2.89	0.567
Stearyl Face Cracks	1.19	1.156

It is apparent from the data that the wet cracking characteristics of the bars are improved by the addition of stearyl alcohol to the formulation.

#### EXAMPLE 4

The aging characteristics of the products were evaluated. Samples of both control and stearyl alcohol bars were cartoned, foil overwrapped and stored at 110° F for four weeks. All bars aged acceptably with no mold growth, off odors or significant color changes observed.

The invention has been described by examples and illustrations thereof but is not to be limited to these because it is evident that one skilled in the art, with the present specification before him would be able to utilize substitutes and equivalents without departing from the invention.

#### Claims

1. A bar soap which is resistant to wet cracking during use comprising about 60 to 85 percent tallow, 15 to 40 percent coco soap chip and 1.5 to 5 percent of a saturated long chain primary alcohol of 16 to 18 carbon atoms in the molecule.
2. A bar soap which is resistant to wet cracking during use which comprises 60 to 85 percent tallow to 15 to 40 percent coco soap chip, 0.01 to 1.0 percent titanium dioxide, 0.01 to 1 percent dye, 5 to 12 percent water and about 1.5 to 5 percent of a long chain primary alcohol of 16 to 18 carbon atoms.
3. The bar soap according to claim 2 wherein the long chain primary alcohol is selected from the group stearyl alcohol and cetyl (1 hexadecanol).
4. A process for manufacturing a bar soap based on about 60 to 85 percent tallow, 15 to 40 percent coco soap chip so as to make it resistant to wet cracking during use which comprises adding a long chain primary alcohol of 16 to 18 carbon atoms in the molecule, titanium dioxide, dye and water to the mixture, milling, plodding, extruding, cutting, and pressing the mixture.
5. The process according to claim 4 which comprises adding 60 to 85 percent tallow 15 to 40 percent coco soap chip, about 1 to 5 percent long chain primary alcohol of 16 to 18 carbon atoms about 0.01 to 1.0 percent titanium dioxide about 0.01 to 1.0 percent dye solution, 5 to 12 percent water milling the mixture plodding the mixture, extruding the plodded mixture, and pressing into bar form.
6. The process according to claim 5 wherein the long chain primary alcohol is selected from the group consisting of stearyl alcohol and cetyl (1 hexadecanol).
7. A process for manufacturing a bar soap based on tallow and coco bar chip so as to make it resistant to wet cracking during use which comprises adding 60 to 85 percent tallow, 15 to 40 percent coco soap chip 1 to 5 percent stearyl alcohol to a mixture of about 0.01 to 1.0 percent titanium dioxide, 0.01 to 1.0 percent

EP 0 413 284 A2

dye and enough water so that the soap bar will contain from about 5 to about 12 percent moisture mixing these ingredients, milling the mixture to ribbon form, plodding, extruding the plodded material into billet form, cutting the billets to the desired lengths and pressing into desired shapes.

5

10

15

20

25

30

35

40

45

50

55



(18)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 413 284 A3**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **90115493.0**

(51) Int. Cl.<sup>5</sup>: **C11D 9/00, C11D 9/04,  
C11D 9/06, C11D 9/26,  
C11D 9/44**

(22) Date of filing: **13.08.90**

(30) Priority: **15.08.89 US 393934**

(43) Date of publication of application:  
**20.02.91 Bulletin 91/08**

(64) Designated Contracting States:  
**AT BE CH DE DK ES FR GB IT LI LU NL SE**

(68) Date of deferred publication of the search report:  
**18.09.91 Bulletin 91/38**

(71) Applicant: **Colgate-Palmolive Company**  
**300 Park Avenue**  
**New York, N.Y. 10022-7499(US)**

(72) Inventor: **Colwell, Dennis J.**  
**One Cornwall Drive**  
**East Windsor, N.J.(US)**  
Inventor: **Pflug, James J.**  
**19 Roanoke Court**  
**Bordentown, N.J.(US)**

(74) Representative: **UEXKÜLL & STOLBERG**  
**Patentanwälte**  
**Beselerstrasse 4**  
**W-2000 Hamburg 52(DE)**

(54) **Bar soap having improved resistance to cracking.**

(57) A bar soap prepared from a tallow-coco soap chip base containing minor amounts of filler, dye and water and from 1 to 5 percent long chain primary alcohol, to reduce or eliminate wet cracking of the bar during use.

**EP 0 413 284 A3**



European  
Patent Office

# EUROPEAN SEARCH REPORT

Application Number

EP 90 11 5493

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	US-A-2 004 874 (W.A. LAZIER) * page 1, lines 28-37; page 2, example 1, lines 71-75; claims 1,7,10 *	1-7	C 11 D 9/00 C 11 D 9/04 C 11 D 9/06 C 11 D 9/26 C 11 D 9/44
Y	DE-A-2 308 098 (HENKEL & CIE.) * pages 6,7, examples 1,2 *	1-7	
Y	DE-A-2 427 986 (HENKEL & CIE.) * claims *; & US-A-401807 (cat. D)	1-7	
A	GB-A-2 142 040 (TAKASAGO PERFUMERY CO.) * whole document *	1-7	
A	GB-A-1 300 415 (UNILEVER LTD.) * page 1, lines 26-29,64,65; claims *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 11 D
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
Berlin		28 June 91	PELLI-WABLAT B
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X : particularly relevant if taken alone</div> <div>Y : particularly relevant if combined with another document of the same category</div> <div>A : technological background</div> <div>O : non-written disclosure</div> <div>P : intermediate document</div> <div>T : theory or principle underlying the invention</div> <div>E : earlier patent document, but published on, or after the filing date</div> <div>D : document cited in the application</div> <div>L : document cited for other reasons</div> <div>&amp; : member of the same patent family, corresponding document</div>			